PATENT SPECIFICATION

(11) 1 506 464

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(21) Application No. 22183/75 (22) Filed 22 May 1975
(31) Convention Application No. 2426266
(32) Filed 29 May 1974 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 5 April 1978
(51) INT CL² C09C 1/48 C04B 27/00
(52) Index at acceptance
C4A K
C1H 120 420 620 711 718 720 754 756 758 771 796

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(54) AQUEOUS CARBON BLACK PREPARATION

(71) We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to aqueous carbon black preparations.

More particularly the invention relates to aqueous carbon-black preparations containing wetting agents for incorporation into mineral binder systems, for example for concrete, roof-tile, exposed concrete, asbestos concrete and external plaster formulations.

These carbon black preparations are used for the permanent, weather-proof black pigmenting of mineral binder systems in which they are incorporated.

It is known that pigment dispersions may be added for colouring purposes to aqueous mineral binder systems, for example a cement-sand mixture, and the binder system subsequently left to set in the usual way. For producing black-coloured systems, it is also known that carbon black dispersions containing wetting agents or dispersants may be added.

Carbon black is produced in various qualities, for example flame black, furnace black and gas or channel black. The differences in particle size, surface structure, surface size, pH-value and density result in differences in the wetting behaviour and dispersibility of the carbon blacks. The wetting agents and dispersants used differ in accordance with these different properties ranging from hydrophilic to hydrophobic. In the case of highly apolar carbon blacks for example, wetting agents are added during the preparation of aqueous carbon black dispersions in order to make the carbophilic surface of the starting carbon black slightly more hydrophilic. In addition, surface-active substances, such as wetting agents or dispersants, are added during the preparation of carbon black dispersions in order optimally to disperse the carbon black used and to stabilise the degree of dispersion.

Anion-active or non-ionic substances such as, for example, alkyl aryl sulphonates, lignosulphonates or polyethylene glycol derivatives, are used as wetting agents or dispersants.

The carbon black dispersions produced in this way are generally liquid, pasty or powdery systems. They may consist, for example, of approximately 35 parts of water, 60 parts of carbon black (pigment) and 5 parts of wetting agent (all parts by weight).

In cases where known carbon black dispersions of this kind are used, it has been found that the weathering properties of correspondingly coloured binder systems, for example roof-tiles, are not altogether satisfactory insofar as the depth of colour at the surface decreases to a considerable extent with prolonged weathering. The reason for this weathering phenomenon has not yet been established. Accordingly, there have been doubts as to whether conventional carbon black dispersions could be used instead of inorganic pigments, such as Fe_3O_4 or iron red oxide, whilst at the same time maintaining a comparable quality standard.

It has now surprisingly been found that, by using certain carbon black preparations preferably produced in powder form, it is possible considerably to improve the weather resistance of mineral binder systems pigmented with carbon black.

The present invention provides an aqueous carbon black preparation for incorporation in a mineral binder system comprising carbon black, water and a fluorine-containing wetting agent.

The invention also provides a mineral binder system, for example a concrete, roof-tile, exposed concrete, asbestos concrete or external plaster formulation containing such a carbon black preparation and a surface or tile prepared by setting or drying such a binder or formulation.

Roof tiles which had been produced by the

same methods on the basis of the same formulations and which only differed in the type of wetting agents or dispersants used, were exposed to weather for more than one year and were subsequently compared with corresponding unused tiles. The roof tiles, in which wetting agents or dispersants corresponding to the prior art had been used, showed a significant reduction in the depth of colour by comparison with the unused tiles. They had faded to a considerable extent.

By contrast, the roof tiles in which wetting agents or dispersants according to the invention had been used, did not show any signs of fading by comparison with the unused tiles. They were identical with the unweathered tiles.

Suitable fluorine-containing wetting agents and dispersants are anion-active and non-ionic agents.

Alkali metal salts of aryl sulphonic acid perfluoroalkene ethers belong to the first group and show a favourable effect. They are obtained, for example, by reacting a perfluoroalkene corresponding to the general formula C_nF_{2n}, in which n is for example $\leqq 10$, preferably $C_{10}F_{20}$, with a polyethylene glycol of the general formula

$$HO—(CH_2—CH_2—O)_m—H,$$

where m in for example $\leqq 23$, preferably with $HO—(CH_2—CH_2—O)_{23}—H$.

The perfluoroalkene corresponding to the general formula C_nF_{2n}, for example with $n=10$, used as starting material in both types of wetting agent is a branched hydrocarbon. It preferably has the structure

$$(C_2F_5)_2(CF_3)C—C(CF_3)=CF(CF_3)$$

with the empirical molecular formula $C_{10}F_{20}$.

In cases where the perfluoroalkene $C_{10}F_{20}$ is used in the production of the alkali metal salts of the aryl sulphonic acid perfluoroethers, the anion-active wetting agent

$$C_{10}F_{19}—O—C_6H_4—SO_3Na$$

is obtained.

A preferred non-ionic wetting agent, prepared with the perfluoroalkene $C_{10}F_{20}$, from the group of polyethylene glycol bis-perfluoroalkene ethers has the structure

$$C_{10}F_{19}—O—(CH_2—CH_2—O)_{23}—C_{10}F_{19}$$

The wetting agents may be used in quantities of from 0.02 to 0.4% and preferably in quantities of from 0.08 to 0.3%, based on the weight of the carbon black. In each individual case, the quantity of wetting agent used is governed by the composition of the binder system and in particular by the type of carbon black used, so that the wetting agents may be used in even larger quantities.

Carbon blacks belonging to the classes LFI (Long Flow Impingement), RCC (Regular Colour Channel), MCF (Medium Colour Furnace), FCFm (Fine Colour Furnace modified), FCF (Fine Colour Furnace) have proved to be particularly suitable for pigmenting concrete roof tiles. It is even possible to use mixtures of these carbon blacks. The use according to the invention of fluorine-containing wetting agents or dispersants guarantees optimum dispersion of the carbon black and stabilises the degree of dispersion in an aqueous carbon black preparation, a wide range existing in regard to the choice of the particular type of carbon black used.

The fluorine-containing wetting agents or dispersants used in accordance with the invention have an extremely favourable influence upon the coloristic appearance i.e. the weathering behaviour of the mineral binders in which the carbon black preparations according to the invention are incorporated. Even after weathering for one year, mineral binders pigmented with carbon black preparations according to the invention retain their colour, as can be seen from the Examples.

The invention is illustrated by comparison with the prior art in the following examples:

I. Preparation of the carbon black preparations

EXAMPLE 1 (prior art)

92 g	of Spezialschwarz 4
1 g	of Vanisperse CB=oxylignins (lignin sulphonate)
5 g	of water
2 g	of Kieselsäure VN 3=precipitated silica
100 g	

The carbon black is introduced into a size 0 edge-runner mill and the requisite quantities of wetting agent and water added over a period of about 5 minutes. This is followed by grinding for 30 minutes.

EXAMPLE 2

80 g	of Spezialschwarz 4
0.2 g	of $C_{10}F_{19}—O—C_6H_4—SO_3Na$
19.8 g	of water
100 g	

This batch is processed in the same way as in Example 1.

EXAMPLE 3

80 g	of Spezialschwarz 4
0.2 g	of $C_{10}F_{19}—O—(CH_2—CH_2—O)_{23}—C_{10}C_{19}$
19.8 g	of water
100 g	

This batch is processed in the same way as in Example 1.

The carbon black, Spezialschwarz 4, used in Examples 1 to 3 has the following characteristics:

Electron microscopic particle diameter	25 mμ
Tamped density DIN 53194.	0.19 g/l
Oil demand FP	300% (g/100g)
pH-value	3
Surface	180 m²/g

It belongs to the LFI Class (Long Flow Impingement).

EXAMPLE 4 (prior art)

92 g of Flammruss 101
1 g of Vanisperse CB=oxylignins (lignin sulphonate)
2 g of Kieselsaure VN 3=precipitated silica
5 g of water

100 g

This mixture is processed in the same way as in Example 1.

EXAMPLE 5

80 g of Flammruss 101
0.2 g of $C_{10}F_{19}—O—C_6H_4—SO_3Na$
19.8 g of water

100 g

This batch is processed in the same way as in Example 1.

EXAMPLE 6

80 g of Flammruss 101
0.2 g of $C_{10}F_{19}—O—(CH_2—CH_2—O)_{22}—C_{10}F_{19}$
19.8 g of water

100 g

This batch is processed in the same way as in Example 1.

The carbon black, Flammruss 101, used in Examples 4 to 6 has the following characteristics:

Electron microscopic particle diameter	95 mμ
Tamped density DIN 53194	0.31 g/l
Oil demand FP	280% (g/100g)
pH-value	7
Surface	21 m²/g

It belongs to the MCF Class (Medium Colour Furnace).

EXAMPLE 7 (prior art)

92 g of Printex A
1 g of Vanisperse CB=oxylignins (lignin sulphonate)
2 g of Kieselsaure VN 3=precipitated silica
5 g of water

100 g

This batch is processed in the same way as described in Example 1.

EXAMPLE 8

80 g of Printex A
0.2 g of $C_{10}F_{10}—O—C_6H_4SO_3Na$
19.8 g of water

100 g

This batch is processed in the same way as described in Example 1.

EXAMPLE 9

80 g of Printex A
0.2 g of $C_{10}F_{10}—O—(CH_2—CH_2O)_{23}—C_{10}F_{19}$
19.8 g of water

100 g

This batch is processed in the same way as in Example 1.

The carbon black, Printex A, used in Examples 7 to 9, has the following characteristics:

Electron microscopic particle diameter	41 mμ
Tamped density DIN 53194	0.30 g/l
Oil demand	300% (g/100g)
pH-value	8
Surface	46 m²/g

It belongs to the MCF Class (Medium Colour Furnace).

EXAMPLE 10 (prior art)

92 g of carbon black (L—TD)
1 g of Vanisperse CB=oxylignins (lignin sulphonate)
2 g of Kieselsaure VN 3=precipitated silica
5 g of water

100 g

This batch is processed in the same way as in Example 1.

EXAMPLE 11

80 g of carbon black (L—TD)
0.2 g of $C_{10}F_{19}—O—C_6H_4—SO_3Na$
19.8 g of water

100 g

This batch is processed in the same way as described in Example 1.

EXAMPLE 12

80 g of carbon black (L—TD)
0.2 g of $C_{10}F_{19}—O—(CH_2—CH_2—O)_{23}—C_{10}F_{19}$
19.8 g of water

100 g

This batch is processed in the same way as in Example 1.

The carbon black, L—TD, used in Examples 10 to 12 has the following characteristics:

Electron microscopic particle diameter	35 mμ
Tamped density DIN 53194	0.17 g/l
Oil demand FP	360% (g/100g)
pH-value	8
Surface	80 m²/g

It belongs to the RCC Class (Regular Colour Channel).

II Production of the Test Tiles

EXAMPLE 13

The following process is used for incorporating the carbon black preparations corresponding to Examples 1 to 12, in mineral binders:

5 g of carbon black preparation corresponding to Examples 1 to 12
100 g of cement (EPZ 275)
300 g of sand (0—3.15 mm)
25 g of water

This batch was mixed in a mortar mixer for 10 minutes.

To produce test tiles, the mixture obtained is introduced into a mould and compressed to form test tiles under an oil pressure of 300 kp/cm².

These test tiles are dried at room temperature (24°C).

In order to test their weathering behaviour, the tiles according to Example 13 were weathered for one year facing south on the roof of an industrial building. The test tiles were compared every 4 months with unweathered comparison tiles. It was found that, after only 4 months, the test tiles according to Examples 1, 4, 7 and 10 were slightly lighter than the unweathered comparison tiles.

Testing after 12 months showed that all the test tiles according to Examples 1, 4, 7 and 10 had faded considerably as a result of weathering by comparison with unweathered tiles. This was not the case with the tiles containing carbon black preparations obtained in accordance with Examples 2, 3, 5, 6, 8, 9, 11 and 12. In their case, the weathered tiles were identical with the unweathered tiles (in regard to depth of colour).

Optical measurements confirm these subjectively obtained results. They were carried out by the spectro-photometric process according to DIN 5033 (using a Zeiss Elrepho spectro-photometer).

The results obtained with a few tiles produced with different wetting agents are shown in the following Table which compares the Y values obtained from the difference between weathered and unweathered tiles.

Wetting Agent Used	Y weathered minus Y unweathered
lignin sulphonate (oxylignin) (Examples 1, 4, 7, 10)	7.4
wetting agent corresponding to Examples 2, 5, 8, 11	1.9
wetting agent corresponding to Examples 3, 6, 9, 12	1.8

EXAMPLE 14

For pigmenting concrete, a carbon black preparation is prepared in a 200 kg batch in accordance with the following recipe using an edge-runner mill:

80 parts of carbon black Printex A
0.1 part of wetting agent $C_{10}F_{19}—O—(CH_2—CH_2—O)_{23}—C_{10}F_{19}$
19.9 parts of water

100 parts (all parts by weight)

The carbon black Printex A has the characteristics specified for Examples 9 to 12.

The carbon black is initially introduced into the edge-runner mill and the wetting agent, previously dissolved in the requisite quantity of water, added over a period of 15 minutes. After the water/wetting agent has been added, the mixture is ground for 60 minutes.

After grinding, the entire batch is ground in a progress hammer mill fitted with screens and subsequently introduced into waterproof, polyethylene-lined bags.

The carbon black preparations which are readily prepared on this scale have the requisite properties. They can be readily incorporated in mineral binder systems, for example concrete systems, which then show the favourable weather resistance.

WHAT WE CLAIM IS:—

1. An aqueous carbon black preparation containing a wetting agent, the preparation comprising carbon black, water and a fluorine-containing wetting agent.

2. A carbon black preparation as claimed in Claim 1, wherein the wetting agent is anion-active.

3. A carbon black preparation as claimed in Claim 1, wherein the wetting agent is non-ionic.

4. A carbon black preparation as claimed in Claim 2, wherein the wetting agent is an alkali metal salt of an aryl sulphonic acid perfluoroalkene ether.

5. A carbon black preparation as claimed in Claim 3, wherein the wetting agent is a polyethylene glycol-bis-perfluoroalkene ether.

6. A carbon black preparation as claimed in any of Claims 1 to 5, containing from 0.02 to 0.4% of wetting agent, based on the weight of carbon black.

7. A carbon black preparation as claimed in Claim 6, containing from 0.08 to 0.3% of wetting agent, based on the weight of carbon black.

8. A carbon black preparation as claimed in any of Claims 1 to 7, wherein the carbon black belongs to the LFI Class (Long Flow Impingement).

9. A carbon black preparation as claimed in any of Claims 1 to 7, wherein the carbon black belongs to the RCC Class (Regular Colour Channel).

10. A carbon black preparation as claimed in any of Claims 1 to 7, wherein the carbon black belongs to the FCFm Class (Fine Colour Furnace modified).

11. A carbon black preparation as claimed in any of Claims 1 to 7, wherein the carbon black belongs to the MCF Class (Medium Colour Furnace).

12. A carbon black preparation as claimed in any of Claims 1 to 7, wherein the carbon black belongs to the FCF Class (Fine Colour Furnace).

13. A carbon black preparation as claimed in any of Claims 1 to 12, wherein at least two carbon blacks are used in admixture with one another.

14. An aqueous carbon black preparation substantially as hereinbefore described with reference to any of Examples 2, 3, 5, 6, 8, 9, 11 or 12.

15. A mineral binder incorporating a carbon black preparation as claimed in any of Claims 1 to 14.

16. A concrete, roof-tile, exposed concrete, asbestos concrete or external-plaster formulation including a carbon black preparation as claimed in any of Claims 1 to 14.

17. A surface or tile prepared by setting or drying a binder or formulation as claimed in Claim 15 or 16.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.